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Quantum Statistics and the Boltzmann Equation

ROBERT M. LEWIS

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Abstract

The system of hierarchy equations for the reduced density operators of quantum statistical mechanics is replaced by a single functional differential equation for a generating functional. A formal solution of the initial value problem for the latter equation is obtained, leading to series expansions of the reduced density operators. These expansions are used to obtain an improved derivation of the quantum-mechanical Boltzmann equation.

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1. Introduction

The statistical-mechanical treatment of a quantum-mechanical many-particle system usually begins with the 'density operator', D_n, which is the solution of an initial value problem for an equation analogous to the classical Liouville equation. The solution of this problem is equivalent to the solution of the quantum-mechanical n-body problem and is therefore not practical when n is large.

In order to circumvent this difficulty one may introduce 'reduced density operators', F_s $(s = 1,2,\ldots)$ which, in an appropriate representation, are defined as integrals of the density cperator. These operators satisfy an infinite system of equation (in the limit $n \to \infty$) called the 'hierarchy equations', and this system is, in turn, equivalent to a single functional differential equation for a 'generating functional', L, which generates the operators F_s.

In Section 4 of this paper we obtain a formal solution of the functional differential equation, and from that solution we derive expansions for the operators F_s as power series in the number density. These expansions have the advantage that for small densities, F_s may be approximated by a few terms of the series. Then to obtain an explicit expression for F_s, only certain k-body problems, where k is small, need to be solved. However the expansions probably suffer from the defect that the remainder terms grow rapidly with time.

The work in Section 4 parallels our earlier work[1] on the corresponding problem in classical mechanics. In fact, by introducing the appropriate representation of the operators, the two treatments become formally almost identical. We call this representation the 'Wigner representation' because in it the density operator is represented by the well-known 'Wigner function'. The Wigner representation is discussed in Section 3.

In Section 2 we review the basic notions of quantum statistical mechanics which we shall require. This is necessary because these notions are presented from a point of view which is slightly different from customary formulations. The unifying idea in this point of view is the representation of Hilbert space in terms of a complete set of commuting observables.

In Section 5 we apply the expansion of F_1, which was derived in Section 4, as the starting point for a derivation of the quantum-mechanical Boltzmann equation. By careful use of operator representations we are able to avoid most of the mathematical difficulties which appear in earlier derivations. However, as we point out in Section 5, one basic difficulty remains in that, at one point, we are forced to argue by analogy with the case of classical mechanics. The significance of this difficulty and the validity of the equation so derived is discussed in the concluding remarks.

2. Basic notions of quantum statistical mechanics

Let $\mathcal{H}$ denote a Hilbert space of elements Φ with inner product (Φ,Φ_1) and norm $\| \Phi \| = (\Phi,\Phi)^{\frac{1}{2}}$. The states of a quantum-mechanical system correspond to elements Φ of $\mathcal{H}$ with $\| \Phi \| = 1$. For many purposes it is convenient to represent the elements Φ by functions $\psi(q) = \psi(q^{(1)},\ldots,q^{(k)})$

such that

$$\int |\psi(q)|^2 dq = \int |\psi(q)|^2 dq^{(1)} \ldots dq^{(k)} < \infty. \tag{2.1}$$

This is the well-known Schroedinger, or coordinate representation. For our purposes it is convenient to indicate the correspondence between elements Φ and functions $\psi(q)$ by writing

$$R_q(\Phi) = \psi(q). \tag{2.2}$$

If $q = \left\{ q^{(1)}, \ldots, q^{(k)} \right\}$ denotes[2] the complete set of co-ordinate operators then

$$R_q(q^{(j)}\Phi) = q^{(j)}\psi(q);\ j = 1, \ldots, k; \tag{2.3}$$

and

$$\| \Phi \|^2 = \int |\psi(q)|^2 dq. \tag{2.4}$$

More generally, if $Y = \left\{ Y^{(1)}, \ldots, Y^{(k)} \right\}$ is any complete set of commuting observables we shall denote the representation of the Hilbert space in terms of these operators by

$$R_Y(\Phi) = c(y) = c(y^{(1)}, \ldots, y^{(k)}) \tag{2.5}$$

$$R_Y(Y^{(j)}\Phi) = y^{(j)}c(y);\ j = 1, \ldots, k. \tag{2.6}$$

Here $c(y)$ is a complex-valued function. In general $\| \Phi \|^2$ will not be given by a simple integral of the type (2.4) but may be given by a sum (discrete spectrum), a combination of an integral and a sum, etc. In order to admit all possibilities we shall write[3]

$$\| \Phi \|^2 = \int |c(y)|^2 dm(y). \tag{2.7}$$

With the aid of the representation R_Y, functions of the operators $Y^{(1)},\ldots,Y^{(k)}$ are conveniently defined by

$$R_Y\left[f(y)\Phi\right] = f(y)c(y) = f(y)R_Y\left[\Phi\right]. \tag{2.8}$$

In this paper we shall be concerned with a system consisting of n identical particles. Since an individual particle can also be considered as a quantum mechanical system it is essential to examine the relationships between the Hilbert spaces of the component systems and the Hilbert space of the composite system.

Given n identical quantum-mechanical systems with Hilbert spaces $\mathcal{H}_\nu$; $\nu = 1,\ldots,n$; let $Y_\nu = \left\{Y_\nu^{(1)},\ldots,Y_\nu^{(k)}\right\}$ be a complete set of commuting observables in $\mathcal{H}_\nu$, with representation

$$R_{Y_\nu}(\Phi_\nu) = c_\nu(y_\nu) = c_\nu(y_\nu^{(1)},\ldots,y_\nu^{(k)}); \tag{2.9}$$

$$\| \Phi_\nu \|^2 = \int \; |c_\nu(y_\nu)|^2 dm(y_\nu). \tag{2.10}$$

Although the subscript ν will be used to distinguish the systems, we choose the operators, and hence the representations, to be the same in the n systems. Let $\mathcal{K}$ be the space of complex-valued functions

$$c(y_{(n)}) = c(y_1,\ldots,y_n) = c(y_1^{(1)},\ldots,y_n^{(k)}) \tag{2.11}$$

for which

$$\int |c(y_{(n)})|^2 dm(y_1)\ldots dm(y_n) < \infty. \tag{2.12}$$

Then $\mathcal{K}$ may be viewed as representing a Hilbert space $\mathcal{H}$ whose elements Φ correspond to the functions $c(y_{(n)})$, and for which

$$\|\Phi\|^2 = \int |c(y_{(n)})|^2 dm(y_1)\ldots dm(y_n). \tag{2.13}$$

We denote this correspondence by

$$R_{Y_{(n)}}(\Phi) = c(y_{(n)}). \tag{2.14}$$

The Hilbert space $\mathcal{H}$ is then said to be the product[7] of the spaces $\mathcal{H}_1, \ldots, \mathcal{H}_n$.

Each observable, A_ν acting on $\mathcal{H}_\nu$ has a representation as a functional operator (e.g. a differential or integral operator) acting on the functions $c_\nu(y_\nu)$. We now define the operator A_ν acting on $\mathcal{H}$ by requiring that the corresponding functional operator acting on the functions $c(y_{(n)})$ be the same functional operator, the variables y_j $(j \neq \nu)$ being held fixed.

The composite of the n identical systems introduced above is the quantum mechanical system whose Hilbert space is the product space $\mathcal{H}$ and whose observables include the operators A_ν just defined, as well as all functions of these. Thus, in constructing the composite system we have identified every physical observable of the component systems with one of the composite system. It is easily seen that the correspondence (2.14) is the representation of $\mathcal{N}$ in terms of the complete set of commuting observables

$$Y_{(n)} = \left\{ Y_1, \ldots, Y_n \right\} = \left\{ Y_1^{(1)}, \ldots, Y_n^{(k)} \right\} . \qquad (2.15)$$

The composite system defined above is called a Maxwell-Boltzmann system to distinguish it from Fermi-Dirac and Bose-Einstein systems to be discussed shortly.

Let P be any permutation of the integers $\left\{ 1, \ldots, n \right\}$. Then P assigns to each integer j in this set another integer Pj in the set. Let $Py_{(n)}$ be defined by

$$Py_{(n)} = P \left\{ y_1, \ldots, y_n \right\} = \left\{ y_{P1}, \ldots, y_{Pn} \right\} . \qquad (2.16)$$

The permutation operator P on $\mathcal{N}$ may now be defined by means of the representation $R_{Y_{(n)}}$:

$$R_{Y_{(n)}}(P\,\Phi) = c(Py_{(n)}). \qquad (2.17)$$

By means of these permutation operators, the symmetry operator $\mathcal{S}_n$ and the anti-symmetry operator $\mathcal{A}_n$ are defined by

$$\mathcal{S}_n = \frac{1}{n!} \sum P \quad ; \quad \mathcal{A}_n = \frac{1}{n!} \sum (\pm) P. \qquad (2.18)$$

Here the summation is over the n! permutations P, and the positive or negative sign is taken for even or odd permutations respectively. It is easy to show that the permutation operators are unitary and that the operators $\mathcal{S}_n$ and $\mathcal{A}_n$ are Hermitian,

$$\mathcal{S}_n^* = \mathcal{S}_n \quad , \quad \mathcal{A}_n^* = \mathcal{A}_n, \tag{2.19}$$

and satisfy the condition

$$\mathcal{S}_n^2 = \mathcal{S}_n \quad , \quad \mathcal{A}_n^2 = \mathcal{A}_n. \tag{2.20}$$

The last two equations imply that $\mathcal{S}_n$ and $\mathcal{A}_n$ are orthogonal projectors.

Let $B = B(A_\nu^{(i)})$ be a function of all the operators $A_\nu^{(i)}$, $\nu = 1,\ldots,n$; $i = 1,\ldots,j_\nu$; where $A_\nu^{(i)}$ is an observable in $\mathcal{H}_\nu$. Then B is an observable in $\mathcal{H}$, and is said to be a symmetric observable if $B(A_{P\nu}^{(i)}) = B(A_\nu^{(i)})$ for all permutations P of $\left\{1,\ldots,n\right\}$. It can easily be shown that an operator B is symmetric if and only if it commutes with all the permutation operators. From this it follows that $\mathcal{S}_n$ and $\mathcal{A}_n$ are symmetric and that any symmetric operator B commutes with $\mathcal{S}_n$ and $\mathcal{A}_n$:

$$\left[B, \mathcal{S}_n\right] = 0 \quad ; \quad \left[B, \mathcal{A}_n\right] = 0. \tag{2.21}$$

Since $\mathcal{S}_n$(or $\mathcal{A}_n$) is an orthogonal projector, we may introduce the subspace $\mathcal{H}_{\mathcal{S}}$ (or $\mathcal{H}_{\mathcal{A}}$) of $\mathcal{H}$ onto which $\mathcal{S}_n$(or $\mathcal{A}_n$) projects. This is the space of all elements Φ of $\mathcal{H}$ for which $\mathcal{S}_n\Phi = \Phi$ (or $\mathcal{A}_n\Phi = \Phi$), i.e., the eigen-space of $\mathcal{S}_n$(or $\mathcal{A}_n$) corresponding to the eigenvalue 1. The elements Φ of $\mathcal{H}_{\mathcal{S}}$ (or $\mathcal{H}_{\mathcal{A}}$) are called symmetric vectors (or anti-symmetric vectors) and have the property that for every permutation operator, P,

$$P\,\Phi = \Phi \qquad (\text{or } P\,\Phi = \pm\ \Phi\,). \tag{2.22}$$

Since every symmetric observable, B, commutes with $\mathcal{S}_n$, it follows that if Φ is an element of $\mathcal{H}_{\mathcal{S}}$ then $B\,\Phi = B\,\mathcal{S}_n\,\Phi = \mathcal{S}_n B\,\Phi$ is also an element of $\mathcal{H}_{\mathcal{S}}$. Hence B is an observable on $\mathcal{H}_{\mathcal{S}}$. The same assertion is true for $\mathcal{H}_{\mathscr{a}}$. Thus we see that there is a natural correspondence between observables in the component systems and symmetric functions of these observables in $\mathcal{H}_{\mathscr{s}}$ and $\mathcal{H}_{\mathscr{a}}$. A quantum mechanical system whose Hilbert space is $\mathcal{H}_{\mathscr{s}}$ (or $\mathcal{H}_{\mathscr{a}}$) and whose observables correspond in the above way to the observables of the component systems is called a Bose-Einstein system (or Fermi-Dirac system).

In the remainder of this paper we shall treat simultaneously the three types of systems mentioned. This is very conveniently doen by introducing the operator Q_n, where $Q_n = \mathscr{s}_n$ for Bose-Einstein systems, $Q_n = \mathscr{a}_n$ for Fermi-Dirac systems, and $Q_n = 1$ for Maxwell-Boltzmann systems. Thus, e.g., $\mathcal{H}_Q = \mathcal{H}$ for the case $Q_n = 1$.

Let $A = A(1,\ldots,j)$ be an operator whose functional representer in the representation $R_{Y_{(n)}}$ is an integral operator acting on the variables $(1,\ldots,j)$, i.e.

$$R_{Y_{(n)}}\left[A(1,\ldots,j)\Phi\right]=\int a(y_1,\ldots,y_j,y_1',\ldots,y_j')c(y_1',\ldots,y_j',y_{j+1},\ldots,y_n) \times dm(y_1')\ldots dm(y_j'). \qquad (2.23)$$

In this case, we say that 'the operator A is represented by the kernel a', and indicate the correspondence by writing[8]

$$R_{Y_{(n)}}\left[A(1,\ldots,j)\right]=a(y_1,\ldots,y_j,y_1',\ldots,y_j')=a(y_{(j)},y_{(j)}'). \qquad (2.24)$$

In terms of the notation introduced in (2.23), $A(2,\ldots,j+1)$ is the operator such that

$$R_{Y_{(n)}}\left[A(2,\ldots,j+1)\Phi\right]=\int a(y_2,\ldots,y_{j+1},y_2',\ldots,y_{j+1}')c(y_1,y_2',\ldots,y_{j+1}',y_{j+2},\ldots,y_n) \times dm(y_2')\ldots dm(y_{j+1}'), \qquad (2.25)$$

etc. It is easy to see that if $A(1,\ldots,j)$ and $B(j+1,\ldots,j+m)$ operate on different sets of variables then $[A,B] = AB - BA = 0$, and

$$R_{Y_{(n)}}[AB] = R_{Y_{(n)}}[A]R_{Y_{(n)}}[B]. \qquad (2.26)$$

Let $\{\Phi_\nu\}$ be a complete orthonormal set of elements of $\mathcal{H}$ and let B be a linear operator on $\mathcal{H}$. The trace of the operator B is defined by[9]

$$\mathrm{Tr}(B) = \sum_\nu (\Phi_\nu, B\,\Phi_\nu), \qquad (2.27)$$

provided the series converges absolutely. It can be shown that the value of $\mathrm{Tr}(B)$ is independent of the choice of the set $\{\Phi_\nu\}$ and if

$$R_{Y_{(n)}}[B] = b(y_{(n)}, y'_{(n)}) \qquad (2.28)$$

then

$$\mathrm{Tr}(B) = \int b(y_{(n)}, y_{(n)})\,dm(y^{(1)})\ldots dm(y^{(n)}). \qquad (2.29)$$

It is convenient also to define the partial trace $T_{s+1,\ldots,j}$ of an operator with respect to some of the variables. Thus, e.g., for $s < j$, $T_{s+1,\ldots,j}A(1,\ldots,j)$ is the operator such that

$$R_{Y_{(n)}}\left\{T_{s+1,\ldots,j}A(1,\ldots,j)\right\} = \int a(y_1,\ldots,y_s,z_{s+1},\ldots,z_j,y'_1,\ldots,y'_s,z_{s+1},\ldots,z_j) \times dm(z_{s+1})\ldots dm(z_j). \qquad (2.30)$$

Of course

$$T_{1,\ldots,n}A(1,\ldots,n) = \mathrm{Tr}A(1,\ldots,n). \qquad (2.31)$$

In quantum statistical mechanics, the mean value of an arbitrary observable, B, is given by

$$\langle B \rangle = \mathrm{Tr}(D_n B) \tag{2.32}$$

where D_n is a non-negative, Hermitian, bounded, completely continuous linear operator, called the density operator. It is normalized by the condition

$$\mathrm{Tr}(D_n) = 1. \tag{2.33}$$

D_n varies with time according to the equation

$$D_n(t) = e^{\frac{-itH_n}{\hbar}} D_n(0)\, e^{\frac{itH_n}{\hbar}} \tag{2.34}$$

where H_n is the Hamiltonian operator of the system. It follows from (2.34) that D_n satisfies the differential equation

$$i\hbar \frac{\partial D_n}{\partial t} = \left[H_n, D_n\right]. \tag{2.35}$$

If, now, we have a quantum mechanical system with Hilbert space $\mathcal{H}_Q$, we must interpret the trace in (2.32) and (2.33) as a trace, $\mathrm{Tr}_{(Q)}$, over $\mathcal{H}_Q$, i.e., the orthonormal set $\left\{\Phi_\nu\right\}$ in (2.27) must consist of elements of $\mathcal{H}_Q$. It is necessary to relate the trace $\mathrm{Tr}_{(Q)}$ to the trace Tr over $\mathcal{H}$, and this can be done as follows:

Let $\left\{\Phi_\nu\right\}$ be a complete orthonormal set in $\mathcal{H}_Q$, and $\left\{\Psi_\mu\right\}$ a complete orthonormal set in the ortho-complement $\mathcal{H}_Q^{\perp}$ of $\mathcal{H}_Q$. Then the combined set is a complete orthonormal set in $\mathcal{H}$, and

$$\mathrm{Tr}(B) = \sum_\nu (\Phi_\nu, B\,\Phi_\nu) + \sum_\mu (\Psi_\mu, B\,\Psi_\mu). \tag{2.36}$$

We assume that B is an observable in $\mathcal{H}_Q$. (Thus in the cases $Q_n = \mathcal{S}_n$ and $Q_n = \mathcal{A}_n$, B is symmetric.) It follows from (2.21) that

$$[B, Q_n] = 0. \tag{2.37}$$

Now $Q_n \Phi_\nu = \Phi_\nu$, $Q_n \Psi_\mu = 0$, and $Q_n^2 = Q_n$. Thus from (2.27) and (2.19)

$$\mathrm{Tr}(Q_n B) = \mathrm{Tr}(Q_n^2 B) = \mathrm{Tr}(Q_n B Q_n) = \sum_\nu (\Phi_\nu, Q_n B Q_n \Phi_\nu)$$

$$= \sum_\nu (Q_n \Phi_\nu, B Q_n \Phi_\nu) = \sum_\nu (\Phi_\nu, B \Phi_\nu) = \mathrm{Tr}_{(Q)}(B). \tag{2.38}$$

Thus in all three cases,

$$\langle B \rangle = \mathrm{Tr}_{(Q)}(D_n B) = \mathrm{Tr}(Q_n D_n B) = \mathrm{Tr}(D_n Q_n B), \tag{2.39}$$

and

$$\mathrm{Tr}(D_n Q_n) = \mathrm{Tr}(Q_n D_n) = 1. \tag{2.40}$$

For a system of n identical components, H_n and D_n are symmetric, hence commute with Q_n. Therefore

$$Q_n D_n(t) = e^{\frac{-itH_n}{\hbar}} \; Q_n D_n(0) \; e^{\frac{itH_n}{\hbar}} \tag{2.41}$$

and

$$i\hbar \frac{\partial}{\partial t} (Q_n D_n) = [H_n, Q_n D_n]. \tag{2.42}$$

The object of quantum statistical mechanics is to calculate the mean values $\langle B \rangle$. To this end, one must study the solutions of the equation

(2.42). Although this can be done in abstract operator notation, or in terms of any convenient representation, we shall work instead with a 'Wigner representation' which we shall introduce in the next section. This representation has the advantage of producing formulas which resemble closely the corresponding formulas of classical statistical mechanics.

The quantum-mechanical system we shall consider consists of n identical monatomic spinless particles contained in a finite volume, V. The particles obey Bose-Einstein, Fermi-Dirac, or Maxwell-Boltzmann 'statistics', according as $Q_n = \mathcal{S}_n$, $Q_n = \mathcal{A}_n$, or $Q_n = 1$. The Hamiltonian of the system is given by

$$\widetilde{H}_n = T_n + U_n + \sum_{i=1}^{n} u_V(q_i), \tag{2.43}$$

$$T_n = \sum_{i=1}^{n} \frac{p_i^2}{2m} = \sum_{i=1}^{n} \sum_{\alpha=1}^{3} \frac{(p_i^\alpha)^2}{2m}, \tag{2.44}$$

$$U_n = \sum_{1 \leqq i < j \leqq n} \phi(|q_i - q_j|). \tag{2.45}$$

Here m denotes the mass of a particle, $q_i = \left\{ q_i^1, q_i^2, q_i^3 \right\}$ and $p_i = \left\{ p_i^1, p_i^2, p_i^3 \right\}$ denote the cartesian coordinates and the conjugate moments of the i^{th} particle, ϕ is the inter-particle potential, and $u_V(q_i)$ is the potential due to the containing boundary. Thus $u_V(q)$ is constant inside V and rapidly approaches infinity at the boundary. At an appropriate point we shall let n and V tend to infinity in such a way that $v = V/n$ approaches a finite limit (the specific volume). In this process, the effect of the terms $u_V(q_i)$ vanishes[10]; hence we shall omit these terms from further equations. The resulting Hamiltonian is

$$H_n = T_n + U_n. \tag{2.46}$$

In our analysis we shall make use of Hamiltonians

$$H_s = T_s + U_s \quad \text{and} \quad H_{s,0} = T_s; \quad s = 1,2,\ldots \tag{2.47}$$

corresponding to systems of s interacting and non-interacting particles.

In what follows we shall make frequent use of a representation in terms of the complete set of momentum operators

$$p_{(n)} = \left\{p_1,\ldots,p_n\right\} = \left\{p_1^1,\ldots,p_n^3\right\}. \tag{2.48}$$

Since this representation will be used so frequently we will denote it simply by R, rather than $R_{p_{(n)}}$. The momentum representation is characterized by

$$R(\Phi) = \phi(p_{(n)}), \tag{2.49}$$

$$R(p_j^\alpha \Phi) = p_j^\alpha \phi(p_n), \tag{2.50}$$

$$\| \Phi \|^2 = \int |\phi(p_{(n)})|^2 dp_{(n)}. \tag{2.51}$$

Here $dp_{(n)} = dp_1 \ldots dp_n = dp_1^1 \ldots dp_n^3$, and the integration is over all values of $p_{(n)}$.

3. The Wigner representation

Let A(1,...,s) be an operator such that

$$R\left[A(1,\ldots,s)\right] = \alpha(p_{(s)},p'_{(s)}). \tag{3.1}$$

Here, as in Section 2, R denotes the momentum-representation. Let

$$a(q_{(s)},p_{(s)}) = (\pi\hbar)^{-3s}\int \exp\left\{\frac{-2i}{\hbar}q_{(s)}\cdot z_{(s)}\right\} \times \alpha(p_{(s)}-z_{(s)},p_{(s)}+z_{(s)})dz_{(s)}. \tag{3.2}$$

It follows, by inversion of the Fourier transform, that

$$\alpha(p_{(s)},p'_{(s)}) = \int \exp\left\{\frac{i}{\hbar}q_{(s)}\cdot(p'_{(s)}-p_{(s)})\right\} \times a\left[q_{(s)},\frac{1}{2}(p_{(s)}+p'_{(s)})\right]dq_{(s)}. \tag{3.3}$$

These equations define a correspondence between functions $a(q_{(s)},p_{(s)})$ and operators A(1,...,s). It is not apparent that a is the representer of the operator A(1,...,s) in terms of any complete set of commuting observables. Nevertheless it is convenient to call a 'the representer of A in a Wigner representation' and to indicate the correspondence by writing

$$W\left[A(1,\ldots,s)\right] = a(q_{(s)},p_{(s)}). \tag{3.4}$$

With the aid of (2.26) it is easy to see that

$$W\left[A(1,\ldots,j)B(j+1,\ldots,j+m)\right] = W\left[A(1,\ldots,j)\right]W\left[B(j+1,\ldots,j+m)\right]. \tag{3.5}$$

For convenience, we shall sometimes denote the pair q,p by x. Thus, e.g.,

$$q_{(s)},p_{(s)} = x_{(s)}; \quad q_1,\ldots,q_s,p_1,\ldots,p_s = x_1,\ldots,x_s; \qquad (3.6)$$

etc.

In terms of the above definitions, the well-known Wigner function, $w_n(t,x_{(n)})$ is simply the Wigner-representer of the operator $Q_n D_n(t)$:

$$w_n(t,x_{(n)}) = w_n(t,q_{(n)},p_{(n)}) = W\left[Q_n D_n(t)\right]. \qquad (3.7)$$

The properties of the Wigner function are discussed extensively in [11]. Here we shall outline briefly those which we shall require.

Since Q_n and D_n are Hermitian and commute, it follows that their product is Hermitian and hence that w is real, although not necessarily non-negative. Given an arbitrary function $g(q_{(n)},p_{(n)})$, it is well known that because of ambiguities arising from the ordering of non-commuting operators there may exist more than one operator corresponding to g. However, among these operators one may specify a unique operator, called the Weyl assignment. If G is the operator corresponding, under this assignment, to $g(q_{(n)},p_{(n)})$ then

$$\langle G \rangle = T_r(Q_n D_n G) = \int w_n(t,q_{(n)},p_{(n)}) g(q_{(n)},p_{(n)}) dq_{(n)} dp_{(n)}. \qquad (3.8)$$

The Weyl assignment and the proof of (3.8) are given in [11].

In classical statistical mechanics, the mean value of a phase function $g(q_{(n)},p_{(n)})$ is given by a formula identical to (3.8) where w_n is the phase space probability density function, and satisfies the

Liouville equation (see [1]). The great virtue of the Wigner function formalism is this similarity to the classical case. Indeed the Wigner function satisfies a 'quantum-mechanical Liouville equation', similar to the classical equation (but differing in the crucial fact that it is not of first order).

This equation is simply the Wigner representation of (2.42) and is given by

$$\frac{\partial w_n}{\partial t} + \left\{ w_n ; T_n \right\} + \sum_{1 \leqq j < k \leqq n} \Theta_{jk} \cdot w_n = 0. \tag{3.9}$$

Here $\left\{ w_n ; T_n \right\}$ denotes the Poisson bracket, and the operator $\Theta_{jk} \cdot$ is given by

$$\Theta_{jk} \cdot w_n = - \frac{2}{\hbar} \sin\left(\frac{\hbar}{2} \nabla_{p_{(n)}} \cdot \nabla_{q_{(n)}} \right) \phi(|q_j - q_k|) w_n(t, r_{(n)}, p_{(n)}) \Big|_{r_{(n)} = q_{(n)}} . \tag{3.10}$$

We note that

$$\begin{aligned} \Theta_{jk} \cdot w_n &= -\nabla_{q_{(n)}} \phi(|q_j - q_k|) \cdot \nabla_{p_{(n)}} w_n(t, q_{(n)}, p_{(n)}) + O(\hbar^2) \\ &= - \left\{ \phi(|q_j - q_k|) ; w_n \right\} + O(\hbar^2). \end{aligned} \tag{3.11}$$

The classical Liouville equation is given by (3.9) with $\Theta_{jk} \cdot w_n$ replaced by $- \left\{ \phi(|q_j - q_k|) ; w_n \right\}$; thus it is clearly the limiting form of the quantum-mechanical equation for $\hbar \to 0$. Various forms of the operator $\Theta_{jk} \cdot$ are given in [11].

With the aid of the Wigner representation, we can introduce a formal solution of (3.9) derived from (2.41). This solution is given in terms of a solution operator $S_t^{(k)}(1,\ldots,k)$ defined as follows: If $a(q_{(s)},p_{(s)}) = W[A(1,\ldots,s)]$, and $k \leq s$ then

$$S_t^{(k)}(1,\ldots,k)a(x_{(s)}) = S_t^{(k)}(1,\ldots,k)a(q_{(s)},p_{(s)})$$

$$= W\left[e^{\frac{it}{\hbar}H_k(1,\ldots,k)}A(1,\ldots,s)e^{-\frac{it}{\hbar}H_k(1,\ldots,k)}\right] . \tag{3.12}$$

Here H_k is defined by (2.47). The solution operator $S_t^{(k,o)}(1,\ldots,k)$ is defined by (3.12) with H_k replaced by $H_{k,o}$. In an analogous way we can define the operator $S_t^{(k)}(2,\ldots,k+1)$, etc. Where no confusion can arise, we omit the explicit indication of the variables. Thus, e.g.,

$$S_t^{(s)}a(q_{(s)},p_{(s)})= S_t^{(s)}(1,\ldots,s)a(q_{(s)},p_{(s)}). \tag{3.13}$$

It follows immediately from the definitions that $S_o^{(k)}a = a$, and for all t_1,t_2

$$S_{t_1}^{(k)}\ S_{t_2}^{(k)} = S_{t_1+t_2}^{(k)}\ a. \tag{3.14}$$

From (2.41) it is clear that the formal solution to the initial value problem for the quantum-mechanical Liousvile equation is given by

$$w_n(t,q_{(n)},p_{(n)}) = S_{-t}^{(n)}\ w_n(0,q_{(n)},p_{(n)}). \tag{3.15}$$

For use in Section 5, it will be convenient to define an operator $\mathcal{Q}_k$ which, in the Wigner representation, corresponds to multiplication of an operator by the operator Q_k. Thus if $a(q_{(s)},p_{(s)}) = W[A(1,\ldots,s)]$, let

$$\mathcal{Q}_k\, a(q_{(s)},p_{(s)}) = W\left[Q_k A(1,\ldots,s)\right]. \tag{3.16}$$

In the case of classical statistical mechanics solution operators may also be defined.[1] One first introduces the solution operator for the system of Hamilton's equations corresponding to the Hamiltonian H_k (or $H_{k,o}$). If we denote the solution of these equations by $x_{(k)}(t) = \left\{q_{(k)}(t),p_{(k)}(t)\right\}$, then this solution operator is defined by

$$S_t^{(k)}\, x_{(k)}(0) = x_{(k)}(t). \tag{3.17}$$

This operator maps each point in 6k-dimensional phase space into its image after time t along the classical trajectory. The classical solution operator for functions is then defined by

$$S_t^{(k)}(1,\ldots,k)a(x_{(s)}) = a\left[S_t^{(k)}x_{(k)},x_{k+1},\ldots,x_s\right], \tag{3.18}$$

$$S_t^{(k)}(2,\ldots,k+1)a(x_{(s)}) = a\left[x_1,S_t^{(k)}\left\{x_2,\ldots,x_{k+1}\right\},x_{k+2},\ldots,x_s\right], \tag{3.19}$$

etc. If, now, we interpret $S_t^{(n)}$ as the classical solution operator, the solution of the initial value problem for the classical Liouville equation is given by (3.15).

It is important to observe that in the case of free particles ($\phi \equiv 0$; $H_n = H_{n,o}$) the classical and quantum-mechanical solution operators coincide. This is seen most easily from the fact that in this case the two Liouville equations are identical.

In both the classical and the quantum-mechanical cases, the determination of the operator $S_t^{(n)}$ is equivalent to the solution of the corresponding mechanical problem and hence is, in general, not practical for $n > 2$. In an attempt to circumvent this difficulty, we introduce 's-particle Wigner functions' defined by

$$f_{n,s}(t,x_{(s)}) = f_{n,s}(t,x_1,\ldots,x_s) = V^s \int w_n(t,x_1,\ldots,x_n)dx_{s+1}\cdots dx_n;$$

$$s = 1,2,\ldots,n. \tag{3.20}$$

By integrating equation (3.9) with respect to $x_{s+1},\ldots,x_n$, one obtains the system of equations for the functions $f_{n,s}$

$$\frac{\partial f_{n,s}}{\partial t} + \left\{f_{n,s};T_s\right\} + \sum_{1\leq j<k\leq s} \theta_{jk}\cdot f_{n,s}$$

$$= -\frac{1-\frac{s}{n}}{v} \sum_{i=1}^{s} \int \theta_{i,s+1}\cdot f_{n,s+1}(t,x_1,\ldots,x_{s+1})dx_{s+1};$$

$$s = 1,2,\ldots,n-1. \tag{3.21}$$

Here T_s is defined by (2.44) and $v = V/n$. We observe that the left side of (3.21) is identical to (3.9) for $s = n$. In the derivation of (3.21) one makes use of the symmetry of w_n, which is a consequence of the symmetry of the operator Q_nD_n. The details of the derivation are given in [11].

In the next section we shall obtain a formal solution of the initial value problem for the system of equations (3.21) in the limit $V \to \infty$, $n \to \infty$, $V/n = v$. In the following section we shall use that solution to derive a quantum-mechanical analogue of the Boltzmann equation.

4. The functional differential equation

The work in this section parallels the development of the classical case given in Sections 2 and 3 of [1]. In fact, if we simply replace the classical density function D_n of [1] by the Wigner function w_n, and the operation $\left\{\phi(|q_j-q_k|);\right\}$ by $-\theta_{jk}\cdot$, the analysis becomes identical. Hence we shall only outline the development here, and refer to [1] for the details.

We begin by introducing the functional

$$L_n[t,u] = \int w_n(t,x_.,\dots,x_n) \prod_{i=1}^{n} \left[1 + vu(x_i)\right]dx_1\dots dx_n, \tag{4.1}$$

which is defined on the domain of functions $u(x)$ for which the integral converges. By functional differentiation we obtain

$$\left.\frac{\delta^s L_n}{\delta u(x_1)\dots\delta u(x_s)}\right|_{u=0} = \frac{n!}{n^s(n-s)!} f_{n,s}(t,x_1,\dots,x_s); \quad s = 0,1,2,\dots,n. \tag{4.2}$$

With the aid of (4.2), L_n may now be expressed as a (finite) series expansion around $u = 0$.

$$L_n[t,u] = 1 + \sum_{s=1}^{n} \frac{1}{s!}\left(1 - \frac{1}{n}\right)\cdots\left(1 - \frac{s-1}{n}\right)$$

$$\times \int f_{n,s}(t,x_1,\ldots,x_s)u(x_1)\ldots u(x_s)dx_1\ldots dx_s. \qquad (4.3)$$

A differential equation for L_n may be obtained by multiplying (3.9) by $\prod_{i=1}^{n}[1 + vu(x_i)]$ and integrating with respect to $x_1,\ldots,x_n$. We then let $n \to \infty$, $V \to \infty$ in the resulting equation. In this process we always assume that $V/n = v$ approaches a finite limit. Thus we obtain

$$\frac{\partial L}{\partial t} = \int \left[u(x_1) + \frac{1}{v}\right]\left[T(p_1); \frac{\delta L}{\delta u(x_1)}\right]dx_1$$

$$- \frac{1}{2}\int \left[u(x_1) + \frac{1}{v}\right]\left[u(x_2) + \frac{1}{v}\right]\theta_{12}\cdot \frac{\delta^2 L}{\delta u(x_1)\delta u(x_2)}\, dx_1 dx_2. \qquad (4.4)$$

Here

$$T(p) = \frac{p^2}{2m} \qquad \text{and} \qquad L[t,u] = \lim_{\substack{n \to \infty \\ V \to \infty}} L_n[t,u]. \qquad (4.5)$$

If we set $f_s(t,x_1,\ldots,x_s) = \lim_{\substack{n\to\infty \\ V\to\infty}} f_{n,s}(t,x_1,\ldots,x_s)$ and pass to the limit in (3.21) and (4.3), we obtain

$$\frac{\partial f_s}{\partial t} + \left\{f_s;T_s\right\} + \sum_{1\leq j<k\leq s} \theta_{jk}\cdot f_s$$

$$= -\frac{1}{v}\sum_{i=1}^{s} \int \theta_{i,s+1}\cdot f_{s+1}(t,x_1,\ldots,x_{s+1})dx_{s+1};$$

$$s = 1,2,\ldots \qquad (4.6)$$

and

$$L[t,u] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int f_s(t,x_1,\ldots,x_s)u(x_1)\ldots u(x_s)dx_1\ldots dx_s. \tag{4.7}$$

It follows from (4.7) that

$$f_s(t,x_1,\ldots,x_s) = \left.\frac{\delta^s L}{\delta u(x_1)\ldots\delta u(x_s)}\right|_{u=o} . \tag{4.8}$$

The equations of the infinite system (4.6) are called the quantum-mechanical hierarchy equations. The functional L is called the generating functional because it generates the functions f_s by means of (4.8).

In order to solve the initial value problem for (4.4), we begin by examining the case of zero density, $1/v = 0$. We shall use superscripts 'o' to denote this case. It is convenient now to denote the independent function by w instead of u. Thus from (4.7), (4.4) and (4.8),

$$L^o[t,w] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int f_s^o(t,x_1,\ldots,x_s)w(x_1)\ldots w(x_s)dx_1\ldots dx_s, \tag{4.9}$$

$$\frac{\partial L^o}{\partial t} - \int w(x_1)\left[T(p_1); \frac{\delta L^o}{\delta w(x_1)}\right]dx_1$$

$$+ \frac{1}{2} \int w(x_1)w(x_2)\theta_{12}\cdot\frac{\delta^2 L^o}{\delta w(x_1)\delta w(x_2)}\, dx_1 dx_2 = 0, \tag{4.10}$$

$$f_s^o(t,x_1,\ldots,x_s) = \left.\frac{\delta^s L^o}{\delta w(x_1)\ldots\delta w(x_s)}\right|_{w=o} ; \tag{4.11}$$

and (4.6) reduces to

$$\frac{\partial f_s^o}{\partial t} + \left\{f_s^o;T_s\right\} + \sum_{1\leq j<k\leq s} \theta_{jk}\cdot f_s^o = 0; \quad s = 1,2,\ldots . \tag{4.12}$$

Comparing (4.12) with (3.9) we observe that f_s^o satisfies the quantum-mechanical Liouville equation for s particles. It follows from (3.15) that the solution of (4.12) is given by

$$f_s^o(t,x_1,\ldots,x_s) = S_{-t}^{(s)} f_s^o(0,x_1,\ldots,x_s); \quad s = 1,2,\ldots \tag{4.13}$$

where $S_t^{(s)}$ is the quantum-mechanical solution operator for a system of s particles. On inserting (4.13) in (4.9) we obtain the solution of (4.10) subject to the initial conditions

$$L^o\left[o,w\right] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int f_s^o(0,x_1,\ldots,x_s)w(x_1)\ldots w(x_s)dx_1\ldots dx_s. \tag{4.14}$$

The $f_s^o(0,x_1,\ldots,x_s)$ are the given initial data.

In order to solve the general equation (4.4) we compare it with (4.10). This comparison suggests that we try a solution of the form

$$L\left[t,u\right] = L^o\left[t,w\right]; \quad w(x) = u(x) + \frac{1}{v}. \tag{4.15}$$

Inserting this expression in (4.4) we see at once that the equation is satisfied by virtue of the fact that L^o satisfies (4.10).

But (4.4) must be solved subject to the initial conditions

$$L[o,u] = \mathscr{L}[u] = 1 + \sum_{s=1}^{\infty} \frac{1}{s!} \int f_s(0,x_1,\dots,x_s)u(x_1)\dots u(x_s)dx_1\dots dx_s . \tag{4.16}$$

The functions $f_s(0,x_1,\dots,x_s)$ are the given initial data. In terms of (4.15) the initial conditions become

$$L^o[o,w] = \mathscr{L}[u]; \quad u = w - \frac{1}{v}. \tag{4.17}$$

Now let $L^o[t,w]$ be the solution of the initial value problem for (4.10) with initial conditions presented in (4.17). Then $L[t,u]$, defined by (4.15), is the solution of the initial value problem for (4.4) with initial conditions presented in (4.16).

One may now obtain expansions of the functions $f_s(t,x_1,\dots,x_s)$ in powers of the density, $1/v$, as follows: From (4.8) and (4.15),

$$f_s(t,x_1,\dots,x_s) = \left.\frac{\delta^s L[t,u]}{\delta u(x_1)\dots\delta u(x_s)}\right|_{u=o} = \left.\frac{\delta^s L^o[t,w]}{\delta w(x_1)\dots\delta w(x_s)}\right|_{w=\frac{1}{v}} . \tag{4.18}$$

If we apply $\delta^s/\delta w(x_1)\dots\delta w(x_s)$ to (4.9) and set $w = 1/v$, we obtain $f_s(t,x_1,\dots,x_s)$ as a power series in $1/v$ with coefficients involving the functions $f_s^o(t,x_1,\dots,x_s) = S_{-t}^{(s)}\ f_s^o(0,x_1,\dots,x_s)$. Now from (4.11) and (4.17)

$$f_s^o(0,x_1,\dots,x_s) = \left.\frac{\delta^s L^o[o,w]}{\delta w(x_1)\dots\delta w(x_s)}\right|_{w=o} = \left.\frac{\delta^s \mathscr{L}[u]}{\delta u(x_1)\dots\delta u(x_s)}\right|_{u=-\frac{1}{v}} \tag{4.19}$$

If We apply $\delta^s/\delta u(x_1)\dots\delta u(x_s)$ to (4.16) and set $u = -1/v$, we obtain $^o_s(0,x_1,\dots,x_s)$ as a power series in $-1/v$ with coefficients involving the functions $f_s(0,x_1,\dots,x_s)$, which are the given initial data. If we now insert the series expression for $f_s^o(0,x_1,\dots,x_s)$ into the series expression for $f_s(t,x_1,\dots,x_s)$ we obtain[13]

$$f_s(t,x_1,\dots,x_s) = \sum_{k=o}^{\infty} \left(\frac{1}{v}\right)^k \int \Bigg[\sum_{j=o}^{k} \frac{(-1)^{k-j}}{j!(k-j)!} S_{-t}^{(j+s)}(1,\dots,j+s)$$

$$\times S_{-t}^{(k-j,o)}(j+s+1,\dots,k+s) f_{k+s}(0,x_1,\dots,x_{k+s})\Bigg]$$

$$\times\, dx_{s+1},\dots,dx_{s+k}; \qquad s = 1,2,\dots\,. \tag{4.20}$$

The series expansion (4.20) for f_s has the advantage that for small densities ($\frac{1}{v} \ll 1$) the function f_s is approximated by terminating the series after a few terms. Now the functions f_s of main interest are those for which s is small, and for these functions, the calculation of the leading terms of the expansion requires a knowledge only of solution operators $S_t^{(k)}$ where k is small, and initial data $f_j(0,x_1,\dots,x_j)$ where j is small. The expansion (4.20) probably suffers, however, from the same defect as the corresponding expansion in the classical case, namely that the remainder terms grow rapidly with time.

In order to obtain the operator analogue of (4.20) we must first introduce 's-particle density operators'

$$F_{n,s}(t,1,\ldots,s) = V^s \, T_{s+1,\ldots,n}\left[Q_n D_n(t)\right], \tag{4.21}$$

and

$$F_s(t,1,\ldots,s) = \lim_{\substack{n \to \infty \\ V \to \infty}} F_{n,s}(t,1,\ldots,s). \tag{4.22}$$

Then it is easy to show that

$$f_s(t,x_1,\ldots,x_s) = W\left[F_s(t,1,\cdots,s)\right] \tag{4.23}$$

and the analogue of (4.20) is

$$\begin{aligned} F_s(t,1,\ldots,s) = \sum_{k=o}^{\infty} \left(\frac{1}{v}\right)^k T_{s+1,\ldots,s+k}\Bigg[\sum_{j=o}^{k} \frac{(-1)^{k-j}}{j!(k-j)!} \\ \times \exp\left\{- \frac{it}{\hbar}\left[H_{j+s}(1,\ldots,j+s) + H_{k-j,o}(j+s+1,\ldots,k+s)\right]\right\} \\ \times F_{k+s}(0,1,\ldots,k+s) \exp\left\{\frac{it}{\hbar}\left[H_{j+s}(1,\ldots,j+s)\right.\right. \\ \left.\left. + H_{k-j,o}(j+s+1,\ldots,k+s)\right]\right\}\Bigg] ; \quad s = 1,2,\ldots \,. \end{aligned} \tag{4.24}$$

In the case of classical mechanics, s-particle density functions are defined as in (3.20), where w_n is replaced by the classical density function. They satisfy a system of hierarchy equations, and the solution of the initial value problem for these equations is given by (4.20) where the solution operators are those appropriate to classical mechanics. These matters are discussed in detail in [1]. In that paper we applied the leading terms of the expansion (4.20) for s = 1 to obtain a simple derivation of the Boltzmann equation. In the next section, we shall attempt to derive the quantum-mechanical analogue of the Boltzmann equation in a similar manner.

5. Derivation of the quantum-mechanical Boltzmann equation

In 1933, Uehling and Uhlenbeck[14] suggested that certain modifications of the collision integral of the classical Boltzmann equation would be appropriate to the case of quantum mechanics. Since that time various authors[10,15,16,17,18,19] have attempted to verify the validity of the resulting equation by deriving it from the basic formulas of quantum statistical mechanics. In our opinion, none of these derivations, including the one to be presented here, is entirely satisfactory. Some of the inconsistencies of the earlier derivations can be removed by proper use of operator representations and application of recent developments in time-dependent scattering theory. The purpose of the present derivation is to remove these inconsistencies and to isolate what we consider to be the real difficulty.

At one point in our derivation we, like the earlier authors, are forced to argue by analogy with the classical case. It is at this point that we feel the basic difficulty remains. After the derivation is completed we shall add some concluding remarks about this difficulty and the possibility of removing it.

The starting point of our derivation is the solution (4.20) of the quantum-mechanical hierarchy equations. Following the suggestion of Kirkwood[20] and others, we shall make use of a time average of f_1. The form of the 'molecular chaos assumption' appropriate to each of our three cases ($Q_n = \mathcal{S}_n$, $Q_n = \mathcal{A}_n$, $Q_n = 1$) may be stated in terms of density operators as follows:

$$F_2(t,1,2) = Q_2 F_1(t,1) F_1(t,2). \tag{5.1}$$

The justification of this assumption is discussed in [10]. We shall assume that it holds for all t. It follows from (3.5), (3.16), and (4.23) that

$$f_2(t,x_1,x_2) = \mathcal{Q}_2 f_1(t,x_1) f_1(t,x_2). \tag{5.2}$$

Thus (5.2) is the Wigner representation of the molecular chaos assumption.

If we set s = 1 in (4.20), we obtain

$$f_1(t,x_1) = S_{-t}^{(1)} f_1(0,x_1) + \frac{1}{v} \int \left[S_{-t}^{(2)} f_2(0,x_1,x_2) - S_{-t}^{(1)}(1) S_{-t}^{(1)}(2) f_2(0,x_1,x_2) \right] dx_2 + O\left(\frac{1}{v^2}\right). \tag{5.3}$$

Since initial values may be specified at an arbitrary time (say at $t - \frac{\tau}{2}$) we obtain, by replacing t by τ,

$$f_1(t + \tfrac{\tau}{2}, x_1) = S^{(1)}_{-\tau} f_1(t - \tfrac{\tau}{2}, x_1) + \frac{1}{v} \int \Big[S^{(2)}_{-\tau} f_2(t - \tfrac{\tau}{2}, x_1, x_2)$$

$$- S^{(1)}_{-\tau}(1) S^{(1)}_{-\tau}(2) f_2(t - \tfrac{\tau}{2}, x_1, x_2) \Big] dx_2 + O\left(\frac{1}{v^2}\right). \qquad (5.4)$$

In a similar manner we obtain

$$f_1(t - \tfrac{\tau}{2}, x_1) = S^{(1)}_{\frac{\tau}{2}} f_1(t, x_1) + O(\tfrac{1}{v}); \quad S^{(1)}_{s} f_1(t+s, x_1) = f_1(t, x_1) + O(\tfrac{1}{v}). \qquad (5.5)$$

If we apply the operator $S^{(1)}_{\frac{\tau}{2}}(1)$ to (5.4) the result is

$$S^{(1)}_{\frac{\tau}{2}} f_1(t + \tfrac{\tau}{2}, x_1) - S^{(1)}_{-\frac{\tau}{2}} f_1(t - \tfrac{\tau}{2}, x_1) = Z, \qquad (5.6)$$

where

$$Z = \frac{1}{v} \int \left[S^{(1)}_{\frac{\tau}{2}}(1) S^{(2)}_{-\tau} f_2(t - \tfrac{\tau}{2}, x_1, x_2) - S^{(1)}_{-\frac{\tau}{2}}(1) S^{(1)}_{-\tau}(2) f_2(t - \tfrac{\tau}{2}, x_1, x_2) \right] dx_2 + O\left(\frac{1}{v^2}\right). \qquad (5.7)$$

We now introduce the transformation of integration variables, $x_2 = S^{(1)}_{\tau/2}\, x_2'$ in (5.7). Since $S^{(1)}_{t} x = S^{(1)}_{t}(q,p) = (q + \frac{t}{m}\, p, p)$ we see that $dx_2' = dx_2$. If we then change x_2' to x_2 in the resulting integral and note that $S^{(2,o)}_{t}(1,2) = S^{(1)}_{t}(1) S^{(1)}_{t}(2)$, we obtain

$$Z = \frac{1}{v} \int \left[S^{(2,o)}_{\frac{\tau}{2}} S^{(2)}_{-\tau} f_2(t - \tfrac{\tau}{2}, x_1, x_2) - S^{(1)}_{-\frac{\tau}{2}}(1) S^{(1)}_{-\frac{\tau}{2}}(2) f_2(t - \tfrac{\tau}{2}, x_1, x_2) \right] dx_2 + O\left(\frac{1}{v^2}\right). \qquad (5.8)$$

From the molecular chaos assumption (5.2), and from (5.5)

$$\begin{aligned} f_2(t-\tfrac{\tau}{2},x_1,x_2) &= \mathcal{Q}_2 f_1(t-\tfrac{\tau}{2},x_1) f_1(t-\tfrac{\tau}{2},x_2) \\ &= \mathcal{Q}_2 S^{(1)}_{\frac{\tau}{2}}(1) f_1(t,x_1) S^{(1)}_{\frac{\tau}{2}}(2) f_1(t,x_2) + 0(\tfrac{1}{v}) \\ &= \mathcal{Q}_2 S^{(2,o)}_{\frac{\tau}{2}} f_1(t,x_1) f_1(t,x_2) + 0(\tfrac{1}{v}). \end{aligned} \qquad (5.9)$$

Thus, since $\mathcal{Q}_2$ commutes with $S^{(2)}_t$ and $S^{(2,o)}_t$

$$Z = \frac{1}{\substack{v\\v}} \int \left[S^{(2,o)}_{\frac{\tau}{2}} S^{(2)}_{-\tau} S^{(2,o)}_{\frac{\tau}{2}} \mathcal{Q}_2 f_1(t,x_1) f_1(t,x_2) - \mathcal{Q}_2 f_1(t,x_1) f_1(t,x_2) \right] dx_2 + 0\left(\frac{1}{v^2}\right).$$

(5.10)

We now introduce a time average, f, of the one-particle Wigner function, f_1, defined by

$$f(t,x_1) = \frac{1}{\tau} \int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} S^{(1)}_s f_1(t+s,x_1)\,ds, \qquad (5.11)$$

and we define the total time derivative of a function $h(t,x_1)$,

$$D_t h(t,x_1) = \frac{d}{dz} S^{(1)}_z h(t+z,x_1) \Big|_{z=o} . \qquad (5.12)$$

Then

$$D_t h(t,x_1) = \frac{d}{dt} h(t+z,q_1 + \frac{z}{m} p_1,p_1) \Big|_{z=o} = \left[\frac{\partial}{\partial t} + \frac{1}{m} p_1 \cdot \nabla_{q_1} \right] h. \qquad (5.13)$$

From (5.11), (5.12) and (5.6),

$$D_t f(t,x_1) = \frac{1}{\tau} \int_{-\frac{\tau}{2}}^{\frac{\tau}{2}} \frac{d}{ds} S_s^{(1)} f_1(t+s,x_1)ds = \frac{1}{\tau} \left[S_{\frac{\tau}{2}}^{(1)} f_1(t+\tfrac{\tau}{2},x_1) - S_{-\frac{\tau}{2}}^{(1)} f_1(t-\tfrac{\tau}{2},x_1) \right]$$

$$= \frac{1}{\tau} Z, \tag{5.14}$$

and from (5.11) and (5.5)

$$f_1(t,x_1) = f(t,x_1) + O(\tfrac{1}{v}). \tag{5.15}$$

If we insert (5.15) into (5.10), and the latter in (5.14) we obtain

$$D_t f(t,x_1) = \frac{1}{\tau v} \int \left[S_{\frac{\tau}{2}}^{(2,0)} S_{-\tau}^{(2)} S_{\frac{\tau}{2}}^{(2,0)} \mathcal{Q}_2 f(t,x_1) f(t,x_2) - \mathcal{Q}_2 f(t,x_1) f(t,x_2) \right] dx_2$$

$$+ O\left(\frac{1}{\tau v^2} \right) . \tag{5.16}$$

We recognize the left side of (5.16) as that of the Boltzmann equation. Our object now will be to transform the right side into the Uehling-Uhlenbeck modification of the collision integral.

So far the analysis in this section is valid for the case of classical mechanics as well as for the case of quantum mechanics, provided we interpret the solution operators according to their classical definition, and take $\mathcal{Q}_2 = 1$. Let us, for the moment, assume that we are dealing with the classical case and examine the solution operators appearing in (5.16). The following discussion depends on the fact that the classical solution operator is defined first for points in phase space (3.17) and then for functions (3.18). With the aid of Figure 1 we examine the effect of the

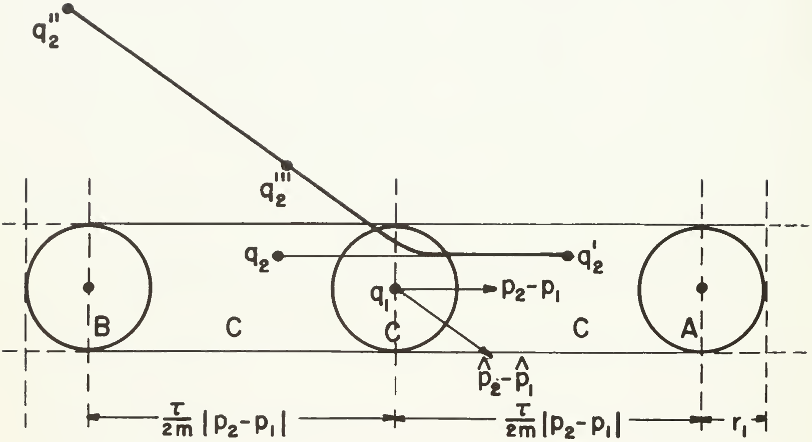

Figure I: CONFIGURATION SPACE FOR CLASSICAL BINARY COLLISION.

operator $S^{(2,o)}_{\tau/2} S^{(2)}_{-\tau} S^{(2,o)}_{\tau/2}$ on points $\left\{x_1,x_2\right\} = \left\{q_1,p_1,q_2,p_2\right\}$ for fixed values of p_1,p_2, and q_1, and various choices of q_2.

In Figure 1, A,B,C together form a cylindrical region with spherical end surfaces. The radius of the cross section of the cylinder is r_1, the interaction distance of the interparticle potential; i.e., we assume that

$$\phi(r) = 0 \text{ for } r \geqq r_1. \tag{5.17}$$

For points q_2 in C, the operator $S^{(2,o)}_{\tau/2}$ maps q_2 to q_2', the position of $S^{(2,o)}_{\tau/2} q_2$ in a coordinate system in which q_1 is fixed. Under $S^{(2,o)}_{\tau/2}$, q_2 moves relative to q_1, a distance $\frac{\tau}{2m}\left|p_2-p_1\right|$ in the direction $p_2- p_1$, along a trajectory which is a straight line because $S^{(2,o)}_{\tau/2}$ corresponds to a Hamiltonian $H_{2,o}$ with no interaction. Then $S^{(2)}_{-\tau}$ maps q_2' to q_2'' along a trajectory which is first straight, then curved in the interaction region (the sphere of radius r_1 about q_1) and then straight, with direction $-(\hat{p}_2- \hat{p}_1)$. Finally $S^{(2,o)}_{\tau/2}$ maps q_2'' back along the straight trajectory with direction $\hat{p}_2- \hat{p}_1$ to q_2''' . The momenta p_1,p_2 are unaffected by the operators $S^{(2,o)}_{\tau/2}$ but are transformed into $\hat{p}_1,\hat{p}_2$ by $S^{(2)}_{-\tau}$. Now if τ is increased, the points q_2' and q_2'' move outward along the straight trajectories but q_2''' does not change its position. Thus for points q_2 in C,

$$S^{(2,o)}_{\frac{\tau}{2}} S^{(2)}_{-\tau} S^{(2,0}_{\frac{\tau}{2}} \left\{x_1,x_2\right\} = \lim_{\tau\to\infty} S^{(2,o)}_{\frac{\tau}{2}} S^{\ (2)}_{-\tau} S^{(2,o)}_{\frac{\tau}{2}} \left\{x_1,x_2\right\}. \tag{5.18}$$

It is easy to see that points outside the region A,B,C simply map into themselves under the operator $S^{(2,o)}_{\tau/2} S^{\ (2)}_{-\tau} S^{(2,o)}_{\tau/2}$. (Of course, the length of the cylindrical region increases linearly with τ.) It follows that the integrand in (5.16) is zero for points q_2 outside the region A,B,C, hence certainly for points in the region

$$|q\cdot\rho| > \frac{\tau}{2m}\,|p_2 - p_1| + r_1 \tag{5.19}$$

where

$$q = q_2 - q_1 \quad ; \quad \rho = \frac{p_2 - p_1}{|p_2 - p_1|}\,. \tag{5.20}$$

Therefore, we can replace $f(t,x_1)f(t,x_2)$ in (5.16) by a function $g(t,q_1,q_2,p_1,p_2)$ where

$$g = \left\{ \begin{array}{l} f\ f \text{ for } |q\cdot\rho| \leqq \frac{\tau}{2m}\,|p_2-p_1| + r_1 \\ \\ 0 \quad \text{for } |q\cdot\rho| > \frac{\tau}{2m}\,|p_2-p_1| + r_1 \end{array} \right\} . \tag{5.21}$$

We now assume that f is spatially homogeneous, i.e., independent of q_1 for all t:

$$f(t,q_1,p_1) = f(t,p_1). \tag{5.22}$$

It follows that g depends on q_1,q_2 only through the value of $(q\cdot\rho)$:

$$g(t,q_1,q_2,p_1,p_2) = g(t,q\cdot\rho,p_1,p_2) = g\left(t,q\cdot\frac{(p_2-p_1)}{|p_2-p_1|},p_1,p_2\right) \tag{5.23}$$

and from (5.21) we may easily derive the identity

$$\frac{1}{\tau V}\int_{-\infty}^{\infty} g(t,q\cdot\rho,p_1,p_2)\,d(q\cdot\rho) = \frac{|p_2-p_1|}{Vm}\,f(t,p_1)f(t,p_2) + O(\tfrac{1}{\tau V}). \tag{5.24}$$

After replacing ff by g in (5.16), we see from (5.18) that we may replace the solution operators by their limiting values (for $\tau \to \infty$) except for q_2 in the spheres A and B (where incomplete collisions occur). The fact that the cylinder increases in length with τ (and in fact becomes infinite for $\tau \to \infty$) is rendered harmless by the fact that g vanishes for $|q \cdot \rho| > \frac{\tau}{2m} |p_2 - p_1| + r_1$. Thus we obtain

$$D_t f(t,p_1) = \frac{1}{\tau v} \int \left[\lim_{\tau\to\infty} S^{(2,0)}_{\frac{\tau}{2}} S^{(2)}_{-\tau} S^{(2,0)}_{\frac{\tau}{2}} \mathcal{Q}_2 g - \mathcal{Q}_2 g \right] dq_2 dp_2 + O(\frac{1}{\tau v}). \quad (5.25)$$

The term $O(\frac{1}{\tau v})$ represents the error due to incomplete collisions.

Although we have derived (5.25) and (5.24) by an argument which is valid only for the case of classical mechanics, we shall nevertheless proceed to show that the Uehling-Uhlenbeck form of the quantum-mechanical Boltzmann equation follows from (5.24) and (5.25) provided the solution operators and the operator $\mathcal{Q}_2$ in the latter are given their quantum-mechanical meaning.

Let G be the operator whose Wigner-representer is g, i.e.

$$W(G) = g(t,q_1,q_2,p_1,p_2). \quad (5.26)$$

Then from (3.16)

$$W(Q_2 G) = \mathcal{Q}_2 g. \quad (5.27)$$

Let

$$a(t,q_1,q_2,p_1,p_2) = \lim_{\tau\to\infty} S^{(2,0)}_{\frac{\tau}{2}} S^{(2)}_{-\tau} S^{(2,0)}_{\frac{\tau}{2}} \mathcal{Q}_2 g - \mathcal{Q}_2 g = W(A). \quad (5.28)$$

Then from our definition of the solution operators (3.12),

$$A = \lim_{\tau\to\infty} e^{\frac{i\tau}{2\hbar} H_{2,o}} e^{-\frac{i\tau}{\hbar} H_2} e^{\frac{i\tau}{2\hbar} H_{2,o}} Q_2 G e^{-\frac{i\tau}{2\hbar} H_{2,o}} e^{\frac{i\tau}{\hbar} H_2} e^{-\frac{i\tau}{2\hbar} H_{2,o}} - Q_2 G. \tag{5.29}$$

Here H_2 and $H_{2,o}$ are the Hamiltonians corresponding to $S_t^{(2)}$ and $S_t^{(2,o)}$, i.e.

$$H_2 = T_2 + U_2 = \frac{1}{2m}(p_1^2 + p_2^2) + \phi(|q_1 - q_2|); \tag{5.30}$$

$$H_{2,o} = T_2 = \frac{1}{2m}(p_1^2 + p_2^2). \tag{5.31}$$

In order to apply the results of scattering theory to (5.29) we introduce center-of-mass and relative coordinates:

$$\left.\begin{array}{l} q_c = \frac{1}{2}(q_1 + q_2)\ ,\ q = q_2 - q_1\ ,\ q_1 = q_c - \frac{1}{2}q\ ,\ q_2 = q_c + \frac{1}{2}q \\ p_c = p_1 + p_2\ ,\ p = \frac{1}{2}(p_2 - p_1)\ ,\ p_1 = \frac{1}{2}p_c - p\ ,\ p_2 = \frac{1}{2}p_c + p \\ M = 2m\ ,\ \mu = \frac{m}{2}\ ,\ H_c = \frac{1}{2M}p_c^2\ ,\ H = E + \phi(|q|)\ ,\ E = \frac{1}{2\mu}p^2 \end{array}\right\} . \tag{5.32}$$

It follows that

$$H_2 = H + H_c \quad ; \quad H_{2,o} = E + H_c. \tag{5.33}$$

From (5.29),

$$A = \lim_{\tau\to\infty} N(\tau) Q_2 G N^*(\tau) - Q_2 G, \tag{5.34}$$

where

$$N(\tau) = e^{\frac{i\tau}{2\hbar} H_{2,o}} e^{-\frac{i\tau}{2\hbar} H_2} e^{-\frac{i\tau}{2\hbar} H_2} e^{\frac{i\tau}{2\hbar} H_{2,o}} = M(\tau)M^*(-\tau). \quad (5.35)$$

Here

$$M(\tau) = e^{\frac{i\tau}{2\hbar} H_{2,o}} e^{-\frac{i\tau}{2\hbar} H_2}. \quad (5.36)$$

Since $\left[E,H_c\right] = 0$ and $\left[H,H_c\right] = 0$, it follows that

$$M(\tau) = e^{\frac{i\tau}{2\hbar}(E+H_c)} e^{-\frac{i\tau}{2\hbar}(H_c+H)} = e^{\frac{i\tau}{2\hbar} E} e^{-\frac{i\tau}{2\hbar} H}. \quad (5.37)$$

From the theory of time-dependent quantum-mechanical scattering,[4,6,21] under appropriate conditions[22] on the 'perturbing operator' $\phi(|q|)$, we have the following result:

$$\lim_{\tau \to \infty} M(\tau) = SU \quad ; \quad \lim_{\tau \to \infty} M(-\tau) = U. \quad (5.38)$$

Here S is the quantum-mechanical scattering operator and U is a unitary operator which transforms the 'unperturbed Hamiltonian' E into the 'perturbed Hamiltonian', H:

$$H = U^*EU \quad ; \quad U\,U^* = U^*U = 1. \quad (5.39)$$

The scattering operator is also unitary, i.e.

$$S\,S^* = S^*S = 1. \quad (5.40)$$

From (5.38)

$$\lim_{\tau \to \infty} M^*(\tau) = U^*S^* \quad ; \quad \lim_{\tau \to \infty} M^*(-\tau) = U^*. \quad (5.41)$$

Thus from (5.35)

$$\lim_{\tau \to \infty} N(\tau) = S\ U\ U^* = S, \tag{5.42}$$

and from (5.34)

$$A = S\ Q_2 G\ S^* - Q_2 G. \tag{5.43}$$

It is somewhat more convenient to work with the operator J = S - 1 instead of the scattering operator S. Thus

$$S = 1 + J, \tag{5.44}$$

and from (5.43),

$$A = J\ Q_2 G + Q_2 G\ J^* + J\ Q_2 G\ J^*. \tag{5.45}$$

From its definition (5.21) we see that g is a symmetric function, i.e. $g(t,x_1,x_2) = g(t,x_2,x_1)$. From this it follows that $G = G(1,2)$ is a symmetric operator, and from (5.42) and (5.35) we see that S and J are symmetric operators, since H_2 and $H_{2,o}$ are. It follows from (2.27) that G and J commute with Q_2. Since $Q_2 = Q_2^2$ and $Q_2^* = Q_2$, (5.45) becomes

$$\begin{aligned} A &= J\ Q_2 G + G(J\ Q_2)^* + J\ Q_2(J\ Q_2)^* \\ &= T\ G + G\ T^* + T\ G\ T^*, \end{aligned} \tag{5.46}$$

where

$$T = J\ Q_2. \tag{5.47}$$

From (5.40) and (5.44)

$$J + J^* = -J\ J^* = -J^* J, \tag{5.48}$$

hence from (5.47)

$$T + T^{*} = -T\,T^{*} = -T^{*}T. \tag{5.49}$$

The operator J is most conveniently discussed by means of the represenation in terms of a complete set of commuting observalbes that includes the unperturbed Hamiltonian, E; hence we shall introduce that representation. To do this, let

$$r = |p| = \frac{1}{2}\,|p_2-p_1| \quad ; \quad \rho = r^{-1}p = \frac{p_2-p_1}{|p_2-p_1|}\;. \tag{5.50}$$

Then ρ is a unit vector, and

$$E = \frac{r^2}{2\mu} = \frac{|p_2-p_1|^2}{8\mu}\;. \tag{5.51}$$

From (5.32) one may determine that the Jacobian of the transformation from p_1, p_2 to p, p_c is 1, i.e.

$$dp_1dp_2 = dpdp_c \tag{5.52}$$

and from (5.50) we see that

$$dp = r^2drdA(\rho). \tag{5.53}$$

Here $dA(\rho)$ is the area element on the unit sphere $|\rho| = 1$. From (5.53) we obtain

$$dp = \lambda^2 dEdA(\rho) \tag{5.54}$$

where

$$\lambda = (2\mu^3E)^{1/4} = (\mu r)^{1/2}. \tag{5.55}$$

In Section 2 we introduced the momentum representation R. Let

$$\phi_o(E,\rho,p_c,p_3,\ldots,p_n) = \lambda\phi(p_1,p_2,p_3,\ldots,p_n) = \lambda R(\,\Phi\,). \tag{5.56}$$

Then from (2.8), (5.32), and (5.51)

$$\lambda R(E\,\Phi) = \lambda\,\frac{p^2}{2\mu}\,\phi(p_1,\ldots,p_n) = E\phi_o(E,\rho,p_c,p_3,\ldots,p_n), \tag{5.57}$$

and from (2.51), (5.52), (5.54), and (5.56)

$$\|\,\Phi\,\|^2 = \int |\phi|^2\lambda^2 dE dA(\rho) dp_c dp_3\ldots dp_n = \int |\phi_o|^2 dE dA(\rho) dp_c dp_3\ldots dp_n. \tag{5.58}$$

(The integrations indicated are, with respect to E over the real semi-axis $0 \leqq E$, with respect to ρ over the unit sphere, and with respect to the vectors $p_c, p_3, \ldots, p_n$ over all space.) It follows from (5.56 - 5.58) that the correspondence (5.56) between elements Φ of $\mathcal{H}$ and functions $\phi_o(E,\rho,p_c,p_3,\ldots,p_n)$ is the representation in terms of the unperturbed Hamiltonian operator E and the operators $\rho, p_c, p_3, \ldots, p_n$. For brevity we denote this representation by R_o. Thus

$$R_o(\,\Phi\,) = \phi_o(E,\rho,p_c,p_3,\ldots,p_n) = \lambda R(\,\Phi\,). \tag{5.59}$$

Now, in terms of the representation R_o, the operator J is given by[4,6,21]

$$R_o(J\,\Phi) = \int j(E,\rho,\rho')\phi_o(E,\rho',p_c,p_3,\ldots,p_n)dA(\rho'), \tag{5.60}$$

and is related to the quantum-mechanical differential scattering cross-

section, $\eta(E,\rho,\rho')$, by

$$\eta(E,\rho,\rho') = (2\pi\hbar)^2 \left| r^{-1} j(E,\rho,\rho') \right|^2. \tag{5.61}$$

The operator J can be put in the form of an integral operator,

$$R_o(J\Phi) = \int j(E,\rho,\rho')\delta(E-E')\delta(p_c-p_c')\delta(p_3-p_3')\cdots\delta(p_n-p_n')\phi_o(E',\rho',p_c',p_3',\cdots,p_n')$$

$$\times\, dE'dA(\rho')dp_c'dp_3'\cdots dp_n', \tag{5.62}$$

with a 'singular kernel'. In earlier treatments, representations of J of the form (5.62) were used, and this led to inconsistencies involving the square of the δ-function. To avoid these difficulties we shall make no use of (5.62) and shall work directly from (5.60).

In the two cases $Q_2 = \mathcal{S}_2$, and $Q_2 = \mathcal{A}_2$, we have, from (2.42),

$$Q_2 = \tfrac{1}{2}(1 \pm P_{1,2}) \tag{5.63}$$

where $P_{1,2}$ is the permutation that interchanges 1 and 2. From (2.17)

$$R\ (Q_2\,\Phi) = \tfrac{1}{2}\Big[\phi_o(p_1,p_2,p_3,\cdots,p_n) \pm \phi(p_2,p_1,p_3,\cdots,p_n)\Big] \tag{5.64}$$

and from (5.56) and (5.50)

$$R_o(Q_2\,\Phi) = \tfrac{1}{2}\Big[\phi_o(E,\rho,p_c,p_3,\cdots,p_n) \pm \phi_o(E,-\rho,p_c,p_3,\cdots,p_n)\Big]. \tag{5.65}$$

Thus, from (5.47) and (5.60)

$$R_o(T\,\Phi) = R_o(J\;Q_2\,\Phi)$$

$$= \frac{1}{2}\int j(E,\rho,\rho')\Big[\phi_o(E,\rho',p_c,p_3,\dots,p_n) \pm \phi_o(E,-\rho',p_c,p_3,\dots,p_n)\Big]dA(\rho')$$

$$= \int b(E,\rho,\rho')\phi_o(E,\rho',p_c,p_3,\dots,p_n)dA(\rho'), \tag{5.66}$$

where

$$b(E,\rho,\rho') = \frac{1}{2}\Big[j(E,\rho,\rho') \pm j(E,\rho,-\rho')\Big]. \tag{5.67}$$

Corresponding to these two cases, we define the symmetrized, and the anti-symmetrized cross-sections

$$\sigma(E,\rho,\rho') = (2\pi\hbar^2)\left|r^{-1}b(E,\rho,\rho')\right|^2 = (2\pi\hbar)^2\left|\frac{1}{2r}\left[j(E,\rho,\rho')\pm j(E,\rho,-\rho')\right]\right|^2. \tag{5.68}$$

Of course, in the case of Maxwell-Boltzmann statistics, $Q_2 = 1$, $T = J$, $b = j$, and $\sigma = \eta$.

From (5.66)

$$R_o(T^*\,\Phi) = \int b^*(E,\rho',\rho)\phi_o(E,\rho',p_c,p_3,\dots,p_n)dA(\rho'), \tag{5.69}$$

and from (5.49) we obtain

$$b(E,\rho,\rho') + b^*(E,\rho',\rho) = -\int b(E,\rho,\rho'')b^*(E,\rho',\rho'')dA(\rho''). \tag{5.70}$$

For $\rho = \rho'$ this becomes

$$b(E,\rho,\rho) + b^*(E,\rho,\rho) = -\int \left|b(E,\rho,\rho')\right|^2 dA(\rho'). \tag{5.71}$$

Our object now is to express the operator A, as given by (5.46) first in R_o-representation and then in R-representation. From the latter it will be easy to transform to Wigner representation and then to evaluate the right side of (5.25) using (5.28). In order to do this, let

$$R(G) = \gamma(p_1, p_2, p_1', p_2') \tag{5.72}$$

and

$$R_o(G) = \gamma_o(E, \rho, p_c, E', \rho'; p_c'), \tag{5.73}$$

i.e.

$$R_o(G\,\Phi) = \int \gamma_o(E, \rho, p_c, E', \rho', p_c')\phi_o(E', \rho', p_c', p_3, \ldots, p_n)dE'dA(\rho')dp_c'. \tag{5.74}$$

Then, from (5.59), (5.56), (5.52), (5.54), and (5.72)

$$\lambda R(G\,\Phi) = R_o(G\,\Phi) = \int \gamma_o(E, \rho, p_c, E', \rho', p_c')\lambda'\phi(p_1', p_2', p_3, \ldots, p_n)(\lambda')^{-2}dp_1'dp_2'$$

$$= \lambda \int \gamma(p_1, p_2, p_1', p_2')\phi(p_1', p_2', p_3, \ldots, p_n)dp_1'dp_2'. \tag{5.75}$$

From this it follows that

$$(\lambda\lambda')^{-1}\gamma_o(E, \rho, p_c, E', \rho', p_c') = \gamma(p_1, p_2, p_1', p_2')$$

$$= \gamma(\tfrac{1}{2}\,p_c - r\rho,\ \tfrac{1}{2}\,p_c + r\rho,\ \tfrac{1}{2}\,p_c' - r'\rho',\ \tfrac{1}{2}\,p_c' + r'\rho'). \tag{5.76}$$

Although γ and γ_o were defined as the R- and R_o- representers of G(1,2), it is clear that (5.76) is an identity which holds for the R- and R_o-representers of an arbitrary operator, B(1,2).

Now from (5.66) and (5.73)

$$R_o(TG\Phi) = \int b(E,\rho,\rho'')\gamma_o(E,\rho'',p_c,E',\rho',p_c')\phi_o(E',\rho',p_c',p_3,\ldots,p_n)$$

$$\times\, dE'dA(\rho')dp_c'dA(\rho''). \tag{5.77}$$

Similarly from (5.69) and (5.73)

$$R_o(GT^*\Phi) = \int b^*(E',\rho',\rho'')\gamma_o(E,\rho,p_c,E',\rho'',p_c')\phi_o(E',\rho',p_c',p_3,\ldots,p_n)$$

$$\times\, dE'dA(\rho')dp_c'dA(\rho''), \tag{5.78}$$

and

$$R_o(TGT^*\Phi) = \int b(E,\rho,\rho''')b^*(E',\rho',\rho'')\gamma_o(E,\rho''',p_c,E',\rho'',p_c')$$

$$\times\, \phi_o(E',\rho',p_c',p_3,\ldots,p_n)dE'dA(\rho')dp_c'dA(\rho'')dA(\rho'''). \tag{5.79}$$

Let $R_o(A) = \alpha_o(E,\rho,p_c,E',\rho',p_c')$. Then from (5.46),

$$\alpha_o(E,\rho,p_c,E',\rho',p_c') = R_o(A) = \int b(E,\rho,\rho'')\gamma_o(E,\rho'',p_c,E',\rho',p_c')dA(\rho'')$$

$$+\int b^*(E',\rho',\rho'')\gamma_o(E,\rho,p_c,E',\rho'',p_c')dA(\rho'')$$

$$+\int b(E,\rho,\rho''')b^*(E',\rho',\rho'')$$

$$\times\, \gamma_o(E,\rho''',p_c,E',\rho'',p_c')dA(\rho'')dA(\rho'''). \tag{5.80}$$

If we set $R(A) = \alpha(p_1,p_2,p_1',p_2')$, then (5.76) is valid for α and α_o as well as for γ and γ_o. Thus from (5.76) and (5.80)

$$\alpha(p_1,p_2,p_1',p_2') = R(A) = \int b(E,\rho,\rho'')\gamma(\tfrac{1}{2}p_c-r\rho'',\tfrac{1}{2}p_c+r\rho'',p_1',p_2')\,dA(\rho'')$$

$$+\int b^*(E',\rho',\rho'')\gamma(p_1,p_2,\tfrac{1}{2}p_c'-r'\rho'',\tfrac{1}{2}p_c'+r'\rho'')\,dA(\rho'')$$

$$+\int b(E,\rho,\rho''')b^*(E',\rho',\rho'')$$

$$\times\,\gamma(\tfrac{1}{2}p_c-r\rho''',\tfrac{1}{2}p_c+r\rho''',\tfrac{1}{2}p_c'-r'\rho'',\tfrac{1}{2}p_c'+r'\rho'')$$

$$\times\,dA(\rho'')dA(\rho'''). \tag{5.81}$$

By definition $\gamma = R(G)$ and $g = W(G)$. Hence from (3.3)

$$\gamma(p_1,p_2,p_1',p_2') = \int e^{\frac{i}{\hbar}\left[s_1\cdot(p_1'-p_1)+s_2\cdot(p_2'-p_2)\right]} g\left[t,s_1,s_2,\tfrac{1}{2}(p_1+p_1'),\tfrac{1}{2}(p_2+p_2')\right]ds_1ds_2. \tag{5.82}$$

We introduce new variables of integration, $s = s_2 - s_1$, $s_c = \frac{1}{2}(s_1 + s_2)$. Then $ds_1ds_2 = dsds_c$, and

$$\gamma(p_1,p_2,p_1',p_2') = \int e^{\frac{i}{\hbar}\left[s_c\cdot(p_1'+p_2'-p_1-p_2)+\frac{1}{2}s\cdot(p_1-p_1'+p_2'-p_2)\right]}$$

$$\times\, g\left[\tfrac{1}{2}(p_1+p_1'),\tfrac{1}{2}(p_2+p_2')\right]dsds_c. \tag{5.83}$$

Here we do not explicitly indicate the dependence of g on t, s, and s_c. But from (5.23) g is independent of s_c; therefore

$$\gamma(p_1,p_2,p_1',p_2') = (2\pi\hbar)^3\delta(p_1'+p_2'-p_1-p_2)\int e^{\frac{i}{2\hbar} s\cdot(p_1-p_1'+p_2'-p_2)}$$

$$\times\ g\left[\tfrac{1}{2}(p_1+p_1'),\tfrac{1}{2}(p_2+p_2')\right]ds. \tag{5.84}$$

If we insert (5.84) in (5.81) we obtain

$$\alpha(p_1,p_2,p_1',p_2')=(2\pi\hbar)^3\delta(p_1'+p_2'-p_1-p_2)\left\{\int b(E,\rho,\rho'')e^{\frac{i}{\hbar} s\cdot(r'\rho'-r\rho'')}\right.$$

$$\times\ g\left[\tfrac{1}{2}(2p_1'+r'\rho'-r\rho''),\tfrac{1}{2}(2p_2'-r'\rho'+r\rho'')\right]ds\,dA(\rho'')$$

$$+\int b^*(E',\rho',\rho'')e^{\frac{i}{\hbar} s\cdot(r'\rho''-r\rho)}$$

$$\times\ g\left[\tfrac{1}{2}(2p_1+r\rho-r'\rho''),\tfrac{1}{2}(2p_2-r\rho+r'\rho'')\right]ds\,dA(\rho'')$$

$$+\int b(E,\rho,\rho''')b^*(E',\rho',\rho'')e^{\frac{i}{\hbar} s\cdot(r'\rho''-r\rho''')}$$

$$\left.\times\ g\left[\tfrac{1}{2}(p_c-r\rho'''-r'\rho''),\tfrac{1}{2}(p_c+r\rho'''+r'\rho'')\right]ds\,dA(\rho'')dA(\rho''')\right\}. \tag{5.85}$$

By definition $\alpha = R(A)$ and $a = W(A)$. Therefore from (3.2)

$$a(t,q_1,q_2,p_1,p_2)=(\pi\hbar)^{-6}\int e^{\frac{-2i}{\hbar}(q_1\cdot z_1+q_2\cdot z_2)}$$

$$\times\ \alpha(p_1-z_1,p_2-z_2,p_1+z_1,p_2+z_2)dz_1dz_2, \tag{5.86}$$

and from (5.25) and (5.28)

$$D_t f(t,p_1) = \frac{1}{\tau v} (\pi\hbar)^{-6} \int e^{\frac{-2i}{\hbar}(q_1\cdot z_1+q_2\cdot z_2)}$$

$$\times\, \alpha(p_1-z_1,p_2-z_2,p_1+z_1,p_2+z_2)\,dz_1dz_2dq_2dp_2 + O(\tfrac{1}{\tau v}). \qquad (5.87)$$

The integrations with respect to q_2 and z_2 may be carried out in (5.87). The result is

$$D_t f(t,p_1) = \frac{1}{\tau v} (\pi\hbar)^{-3} \int e^{\frac{-2i}{\hbar}q_1\cdot z} \alpha(p_1-z,p_2,p_1+z,p_2)\,dz\,dp_2 + O(\tfrac{1}{\tau v}). \qquad (5.88)$$

We now insert (5.85) in (5.88). In so doing we replace p_1 by p_1-z, p_1' by p_1+z, and p_2' by p_2. Then $\delta(p_1'+p_2'-p_1-p_2)$ becomes $\delta(2z) = 2^{-3}\delta(z)$. The result is

$$\begin{aligned} D_t f(t,p_1) = \frac{1}{\tau v} \Bigg\{ &\int b(E,\rho,\rho')e^{\frac{ir}{\hbar}s\cdot(\rho-\rho')} g\left[t,s\cdot\frac{(\rho+\rho')}{|\rho+\rho'|},p_1+\frac{r}{2}(\rho-\rho'),p_2-\frac{r}{2}(\rho-\rho')\right] \\ &\times dsdA(\rho')dp_2 + \int b^*(E,\rho,\rho')e^{\frac{-ir}{\hbar}s\cdot(\rho-\rho')} \\ &\times g\left[t,s\cdot\frac{(\rho+\rho')}{|\rho+\rho'|},p_1+\frac{r}{2}(\rho-\rho'),p_2-\frac{r}{2}(\rho-\rho')\right]dsdA(\rho')dp_2 \\ &+\int b(E,\rho,\rho'')b^*(E,\rho,\rho')e^{\frac{ir}{\hbar}s\cdot(\rho'-\rho'')} \\ &\times g\left[t,s\cdot\frac{(\rho'+\rho'')}{|\rho'+\rho''|},\frac{p_c}{2}-\frac{r}{2}(\rho''+\rho'),\frac{p_c}{2}+\frac{r}{2}(\rho''+\rho')\right]dsdA(\rho')dA(\rho'')dp_2\Bigg\} + O(\tfrac{1}{\tau v}). \end{aligned}$$

(5.89)

In (5.89) we have indicated explicitly the dependence of g on t and s. This dependence is obtained from (5.23).

From (5.32), $p_2 = p_1 + 2p$. Therefore, for fixed p_1,

$$dp_2 = 2^3 dp = 2^3 r^2 dr dA(\rho). \tag{5.90}$$

If we use (5.90) to replace dp_2 in (5.89), we may then use the result (A.1),(A.36) of the Appendix to simplify (5.89). This yields

$$\begin{aligned} D_t f(t,p_1) = \frac{(2\pi h)^2}{\tau V} \Bigg\{ & \int r^{-2} b(E,\rho,\rho) g\left[t, s\cdot\rho, p_1, p_2\right] d(s\cdot\rho) dp_2 \\ & + \int r^{-2} b^*(E,\rho,\rho) g\left[t, s\cdot\rho, p_1, p_2\right] d(s\cdot\rho) dp_2 \\ & + \int r^{-2} b(E,\rho,\rho') b^*(E,\rho,\rho') g\left[t, s\cdot\rho', \hat{p}_1, \hat{p}_2\right] \\ & \times d(s\cdot\rho') dA(\rho') dp_2 \Bigg\} + O\left(\frac{1}{\tau V}\right). \end{aligned} \tag{5.91}$$

Here

$$\hat{p}_1 = \frac{p_c}{2} - r\rho' = p_1 + r(\rho-\rho'), \quad \hat{p}_2 = \frac{p_c}{2} + r\rho' = p_2 - r(\rho-\rho'). \tag{5.92}$$

Let $\hat{p} = \frac{1}{2}(\hat{p}_2 - \hat{p}_1) = r\rho'$. From (5.92) we easily determine that $\hat{p}_1 + \hat{p}_2 = p_1 + p_2$ and $\hat{p}_1^{\,2} + \hat{p}_2^{\,2} = p_1^{\,2} + p_2^{\,2}$. Thus $\hat{p}_1$ and $\hat{p}_2$ are the final momenta after a collision of two particles whose initial momenta are p_1 and p_2. The final relative momentum is $\hat{p}$ and the final relative direction is ρ'. The collision preserves total momentum and the kinetic energy of both the total and relative motions.

We now use (5.71) to simplify (5.91). Thus we obtain

$$D_t f(t,p_1) = \frac{(2\pi\hbar)^2}{\tau V} \int r^{-2} |b(E,\rho,\rho')|^2 \left\{ \int g(t,s\cdot\rho',\hat{p}_1,\hat{p}_2) d(s\cdot\rho') \right.$$

$$\left. - \int g(t,s\cdot\rho,p_1,p_2) d(s\cdot\rho) \right\} dA(\rho') dp_2 + O(\tfrac{1}{\tau V}). \tag{5.93}$$

Finally, from (5.24) and (5.68),

$$D_t f(t,p_1) = \frac{1}{V} \int \sigma(E,\rho,\rho') \left[f(t,\hat{p}_1) f(t,\hat{p}_2) - f(t,p_1) f(t,p_2) \right]$$

$$\times \left| \frac{p_2 - p_1}{m} \right| dA(\rho') dp_2 + O(\tfrac{1}{\tau V}). \tag{5.94}$$

For sufficiently large τ, we may neglect the remainder term in (5.94) and the result is the Uehling-Uhlenbeck form of the quantum-mechanical Boltzmann equation, for the spatially homogeneous case. The Uehling-Uhlenbeck equation for the inhomogeneous case is given by

$$D_t f(t,q_1,p_1) = \frac{1}{V} \int \sigma(E,\rho,\rho') \left[f(t,q_1,\hat{p}_1) f(t,q_1,\hat{p}_2) - f(t,q_1,p_1) f(t,q_1,p_2) \right]$$

$$\times \left| \frac{p_2 - p_1}{m} \right| dA(\rho') dp_2. \tag{5.95}$$

The derivation of (5.95) would require further work.

Conclusion:

It is quite clear that the weak point in the present derivation is the argument leading to (5.25) and (5.24) which proceeds by analogy with the classical case. In fact, in our opinion, this point is so weak that it leaves the validity of the result, (5.94), in considerable doubt. In recent years, some work has been done[23] to clarify the asymptotic approach (as t → ∞) of the operator $\exp(\frac{it}{\hbar} E)\exp(\frac{-it}{\hbar} H)$ to the operator SU, as in (5.38). It may be that this type of study will resolve the difficulty that we have pointed out.

Appendix

The purpose of this section is to apply the formula for the inversion of Fourier transforms in order to simplify integrals of the form

$$I \doteq \int e^{\frac{ir}{\hbar} s\cdot(\rho-\omega)} F\left[s\cdot\frac{\rho+\omega}{|\rho+\omega|}, \rho, \omega\right] dA(\rho)dA(\omega)ds. \tag{A.1}$$

Here ρ and ω are unit vectors and dA is the area element on the unit sphere. We shall make use of the Fourier inverse relation in the form

$$\int e^{\pm\frac{ir}{\hbar} y(x-x')} f(x')dx'dy = \frac{2\pi\hbar}{r} f(x). \tag{A.2}$$

The area element dA can be replaced by an area element in the plane by introducing a cartesian coordinate system such that ρ has components $\rho = (\rho_1, \rho_2, \rho_3)$; $\rho_1^2 + \rho_2^2 + \rho_3^2 = 1$. Then

$$dA(\rho) = \frac{d\rho_1 d\rho_2}{|\rho_3|} . \tag{A.3}$$

To transform the integral I, we introduce a vector

$$\tau = \rho - \omega \tag{A.4}$$

and a unit vector

$$\sigma = \frac{\rho + \omega}{|\rho + \omega|} . \tag{A.5}$$

Then

$$\sigma \cdot \tau = 0. \tag{A.6}$$

Let

$$j_4 = (\sigma_1^2 + \sigma_2^2)^{-1/2}(\sigma_2, -\sigma_1, 0), \tag{A.7}$$

$$j_5 = \sigma \times j_4 = (\sigma_1^2 + \sigma_2^2)^{-1/2}(\sigma_1\sigma_3, \sigma_2\sigma_3, -\sigma_1^2-\sigma_2^2), \tag{A.8}$$

$$j_6 = \sigma. \tag{A.9}$$

j_4, j_5, and j_6 form an orthonormal basis. Since $\sigma \cdot \tau = 0$,

$$\tau = \tau_4 j_4 + \tau_5 j_5 \tag{A.10}$$

where

$$\tau_4 = \tau \cdot j_4 = B^{-1/2}\Big[\sigma_2(\rho_1-\omega_1) - \sigma_1(\rho_2-\omega_2)\Big], \tag{A.11}$$

$$\tau_5 = \tau \cdot j_5 = B^{-1/2}\Big[\sigma_1\sigma_3(\rho_1-\omega_1)+\sigma_2\sigma_3(\rho_2-\omega_2)-B(\rho_3-\omega_3)\Big], \tag{A.12}$$

$$B = \sigma_1^2 + \sigma_2^2. \tag{A.13}$$

Let

$$A = (\rho+\omega)^2 = 2(1+\rho\cdot\omega) = 2(1+\rho_1\omega_1+\rho_2\ {}_2+\rho_3\omega_3). \tag{A.14}$$

Then

$$\sigma_1 = A^{-1/2}(\rho_1+\omega_1), \qquad \sigma_2 = A^{-1/2}(\rho_2+\omega_2) \tag{A.15}$$

$$B = A^{-1}\Big[\rho_1^2+2\rho_1\omega_1+\omega_1^2+\rho_2^2+2\rho_2\omega_2+\omega_2^2\Big]. \tag{A.16}$$

We proceed to calculate the Jacobian of the transformation from ρ and ω to τ and σ, evaluating the results only at $\tau = 0$, i.e. at $\rho = \omega = \sigma$. By using relations of the form

$$\frac{\partial\rho_3}{\partial\rho_1} = -\frac{\rho_1}{\rho_3} \tag{A.17}$$

we successively obtain, at $\tau = 0$,

$$A = 4, \tag{A.18}$$

$$\frac{\partial A}{\partial\rho_1} = \frac{\partial A}{\partial\rho_2} = \frac{\partial A}{\partial\omega_1} = \frac{\partial A}{\partial\omega_2} = 0, \tag{A.19}$$

$$\frac{\partial\sigma_1}{\partial\rho_1} = \frac{\partial\sigma_1}{\partial\omega_1} = \frac{\partial\sigma_2}{\partial\rho_2} = \frac{\partial\sigma_2}{\partial\omega_2} = \frac{1}{2}, \tag{A.20}$$

$$\frac{\partial\sigma_1}{\partial\rho_2} = \frac{\partial\sigma_1}{\partial\omega_2} = \frac{\partial\sigma_2}{\partial\rho_1} = \frac{\partial\sigma_2}{\partial\omega_1} = 0, \tag{A.21}$$

$$\frac{\partial B}{\partial\rho_1} = \frac{\partial B}{\partial\omega_1} = \sigma_1, \qquad \frac{\partial B}{\partial\rho_2} = \frac{\partial B}{\partial\omega_2} = \sigma_2, \tag{A.22}$$

$$\left.\begin{aligned} \frac{\partial\tau_4}{\partial\rho_1} &= B^{-1/2}\sigma_2, & \frac{\partial\tau_4}{\partial\rho_2} &= -B^{-1/2}\sigma_1, \\ \frac{\partial\tau_4}{\partial\omega_1} &= -B^{-1/2}\sigma_2, & \frac{\partial\tau_4}{\partial\omega_2} &= B^{-1/2}\sigma_1, \end{aligned}\right\} \tag{A.23}$$

$$\frac{\partial\tau_5}{\partial\rho_1} = C\sigma_1, \quad \frac{\partial\tau_5}{\partial\rho_2} = C\sigma_2, \quad \frac{\partial\tau_5}{\partial\omega_1} = -C\sigma_1, \quad \frac{\partial\tau_5}{\partial\omega_2} = -C\sigma_2, \tag{A.24}$$

where

$$C = B^{-1/2}\sigma_3 + B^{1/2}\sigma_3^{-1}. \tag{A.25}$$

Let

$$J_1 = \frac{d\sigma_1 d\sigma_2 d\tau_4 d\tau_5}{d\rho_1 d\rho_2 d\omega_1 d\omega_2} = \left| \begin{vmatrix} \frac{\partial\sigma_1}{\partial\rho_1} & \frac{\partial\sigma_1}{\partial\rho_2} & \frac{\partial\sigma_1}{\partial\omega_1} & \frac{\partial\sigma_1}{\partial\omega_2} \\ \frac{\partial\sigma_2}{\partial\rho_1} & \frac{\partial\sigma_2}{\partial\rho_2} & \frac{\partial\sigma_2}{\partial\omega_1} & \frac{\partial\sigma_2}{\partial\omega_2} \\ \frac{\partial\tau_4}{\partial\rho_1} & \frac{\partial\tau_4}{\partial\rho_2} & \frac{\partial\tau_4}{\partial\omega_1} & \frac{\partial\tau_4}{\partial\omega_2} \\ \frac{\partial\tau_5}{\partial\rho_1} & \frac{\partial\tau_5}{\partial\rho_2} & \frac{\partial\tau_5}{\partial\omega_1} & \frac{\partial\tau_5}{\partial\omega_2} \end{vmatrix} \right|. \tag{A.26}$$

If we insert (A.20), (A.21), (A.23), and (A.24) in (A.26) we obtain easily, at $\tau = 0$,

$$J_1 = \frac{1}{|\sigma_3|} . \tag{A.27}$$

Let J be defined by

$$dA(\rho)dA(\omega) = J d\tau_4 d\tau_5 dA(\sigma). \tag{A.28}$$

Then from (A.3),

$$\frac{d\rho_1 d\rho_2 d\omega_1 d\omega_2}{|\rho_3|\ |\omega_3|} = J\ d\tau_4 d\tau_5 \frac{d\sigma_1 d\sigma_2}{|\sigma_3|} , \tag{A.29}$$

and, at $\tau = 0$,

$$J = \frac{|\sigma_3|}{|\rho_3|\ |\omega_3|} J_1^{-1} = 1. \tag{A.30}$$

Now define F to be zero in (A.1) for $|\rho| \neq 1$ or $|\omega| \neq 1$. The integral may be written as a sum of four terms depending on the domain of integration,

$$I_{++}(\rho_3 > 0, \omega_3 > 0), I_{--}(\rho_3 < 0, \omega_3 < 0), I_{+-}(\rho_3 > 0, \omega_3 < 0), I_{-+}(\rho_3 < 0, \omega_3 > 0) \tag{A.31}$$

and by (A.28)

$$I = \int e^{\frac{ir}{\hbar} s\cdot\tau} F[s\cdot\sigma, \rho, \omega] J d\tau_4 d\tau_5 dA(\sigma) ds. \tag{A.32}$$

In the transformed terms, I_{++} corresponds to $\sigma_3 > 0$, and I_{--} to $\sigma_3 < 0$, and the τ-domains of both of these integrals include the point $\tau = 0$. The τ-domains for I_{+-} and I_{-+} exclude the point $\tau = 0$. (A.32) may be written

$$I = \int e^{\frac{ir}{\hbar}\left[s_4\tau_4 + s_5\tau_5\right]} F[s_6, \rho, \omega] J ds_6 ds_4 ds_5 d\tau_4 d\tau_5 dA(\sigma), \tag{A.33}$$

and from (A.2)

$$I = \left(\frac{2\pi\hbar}{r}\right)^2 \int F[s_6, \rho, \omega] J ds_6 \Big|_{\tau=0} dA(\sigma). \tag{A.34}$$

But at $\tau = 0$, $\rho = \omega = \sigma$ and $J = 1$; hence

$$I = \left(\frac{2\pi\hbar}{r}\right)^2 \int F\left[s_6, \sigma, \sigma\right] ds_6 dA(\sigma). \tag{A.35}$$

Since the point $\tau = 0$ is outside the domain of integration, $I_{+-} = I_{-+} = 0$. The contributions I_{++} and I_{--} may be added to produce an integral over the entire unit sphere $|\sigma| = 1$. By changing σ to ρ, we obtain the result

$$I = \left(\frac{2\pi\hbar}{r}\right)^2 \int F\left[(s\cdot\rho), \rho, \rho\right] d(s\cdot\rho) dA(\rho). \tag{A.36}$$

Footnotes and References

[1] R.M. Lewis, J. Math. Phys., $\underline{2}$, 222 (1961).

[2] Following customary notation we sometimes use the same symbol to denote an operator and the independent variable (eigenvalue) in its representation.

[3] In a rigorous treatment of quantum mechanics, R_Y is called the 'simultaneous spectral representation' of the complete set of commuting operators $Y^{(1)},\dots,Y^{(k)}$, and $m(y)$ is a measure function. For an excellent treatment of these notions see [4-6].

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[8] It is important to note the distinction between (2.14) and (2.24). The former is a correspondence between elements $\underline{\Phi}$ and functions $\underline{c}$; the latter is a correspondence between operators A and kernels $\underline{a}$, which is induced by the former.

[9] John von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton University Press, 1955) pp. 178-195.

[10] See N.N. Bogolyubov and K.P. Gurov, J. Exptl. Theoret. Phys. (U.S.S.R.) 17, 614 (1947).

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[13] Except for slight differences of notation, (4.20) is identical to equation (38) of [1]. The latter was obtained by a process somewhat more involved than the one indicated here, in order to avoid introducing divergent integrals at an intermediate step.

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[22] The conditions given in [4] and [6] are such as to exclude point eigenvalues of H. In [21] the theory is extended to include point eigenvalues.

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